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Chemical fractionation of zinc versus cadmium among other metals nickel, copper and lead in the northern North Sea

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Abstract

Concentrations of dissolved Ni, Cu, Zn, Cd and Pb were measured in water samples collected during a cruise with R.V Pelagia (29-6/14-7-1993) in the northern North Sea and N.E. Atlantic Ocean. At least six depths (0–90 m) were sampled with modified Go-Flo samplers from a rubber zodiac. In the study area, the first 25 m were well mixed and stratification occurred below this depth. The local bloom of *Emiliania huxleyi* hardly affected the trace metals concentration, except for some removal of Cd as seen from its correlation with nitrate. The mean dissolved concentrations were for Ni (3.66 nM), Cu (1.61 nM), Zn (4.5 nM), Cd (48 pM) and Pb (108 pM). These concentrations are among the lowest reported for the North Sea and are of similar magnitude to those found in the eastern North Atlantic at the same latitude. Zn was the only exception with values 10 times higher compared to those in the Atlantic Ocean, suggesting external inputs, mainly atmospheric and possibly from surrounding land masses. The observed ratio Zn:Cd in the North Sea and estuaries is in between the high ratio 600–900 for continental sources and the low ratio 5–10 for oceanic waters. Latter low ratio is consistent with the 21-fold stronger inorganic complexation of Cd in seawater which, in combination with the preferential biological uptake of Zn, may lead to the observed about hundredfold fractionation of Zn versus Cd in the marine system. Other processes may play a role but would need further investigation. The dissolved Pb values tend to be lower than found before in the North Sea, indicating decreasing inventories due to reduced anthropogenic emissions.

Keywords: fractionation Zn and Cd; Ni; Cu; Pb; North Sea

1. Introduction

In recent years, progress has been made in the study of the distribution, behaviour and concentration of dissolved trace metals in the North Sea (e.g., Duinker and Nolting, 1982; Jones and Jefferies, 1983; Balls, 1985a,b; Brügmann et al., 1985; Danielsson et al., 1985; Kremling, 1985; Nolting, 1986; Kremling et al., 1987; Kremling and Hydes, 1988; Fileman et al., 1991; Tappin et al., 1993; Tappin et al., 1995). Most of these studies of the North Sea and coastal seas all over the world were, however, focusing on the coastal zones and near densely populated countries, in our case on the shallow southern part of the North Sea. This is not surprising, because in general those studies were related to river inputs and/or

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pollution sources. In general, trace metals have not been well studied in the more offshore, remote, and deeper parts of coastal seas.

The northern North Sea beyond 59°N latitude is between 100 and 200 m deep (Fig. 1) and has a vigorous exchange with the North Atlantic Ocean. This accounts for some 90% of all exchange of the complete North Sea, the remaining about 10% taking place at the Straits of Dover (Otto et al., 1990; Hoppema and de Baar, 1992). The exchanges are highly variable due to wind forcing of tides and currents and, therefore, also strongly seasonal. Nevertheless, the average residence time of the water in the whole North Sea is estimated at about 1 year, with much shorter exchange time less than 6 months at the northern sites of our research area (Fig. 1). In the northern North Sea, few trace metal studies have been reported (Balls, 1985a; Kremling et al., 1987),

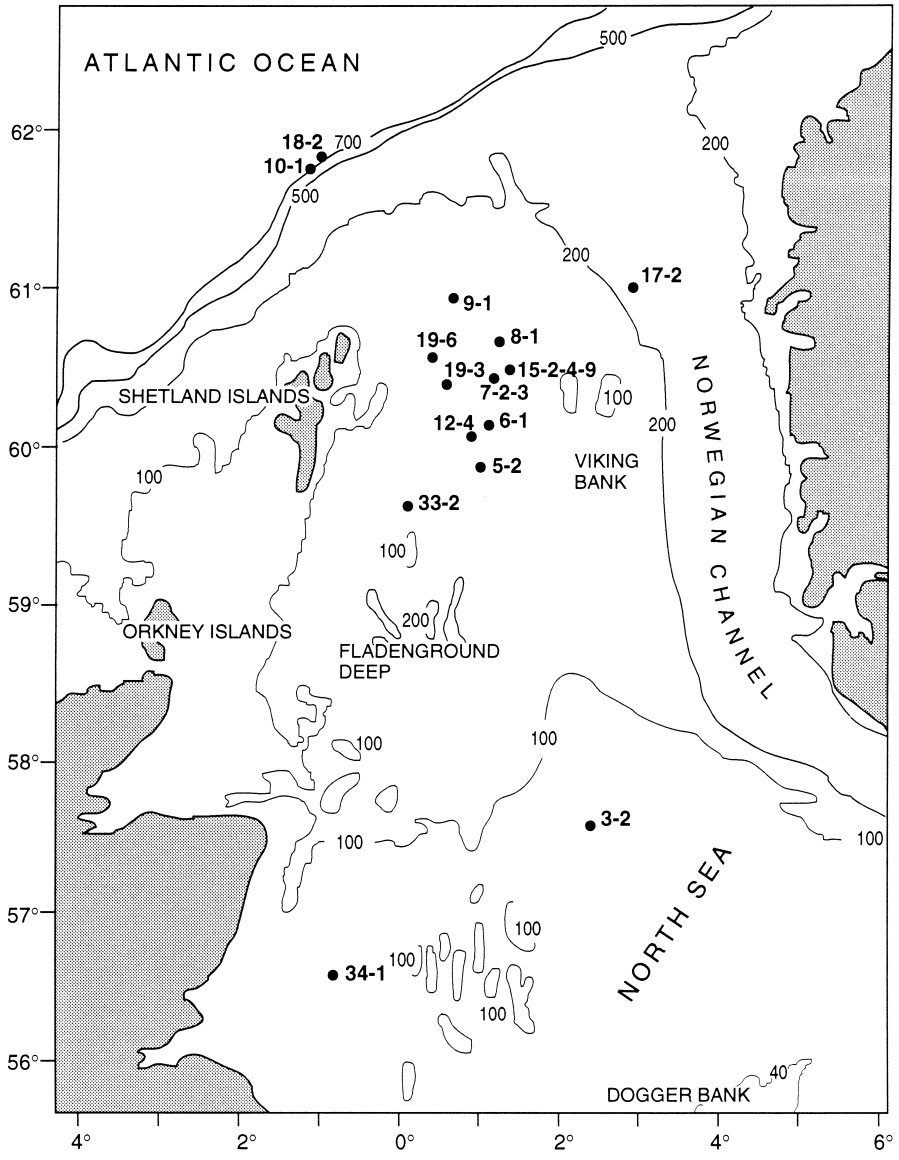

Fig. 1. Chart with sampling stations in the North Sea.

especially for Pb and Zn only one previous study is known (Brügmann et al., 1985). Collection of data of Ni, Cu, Zn, Cd and Pb for this part of the North Sea was deemed worthwhile for (i) unraveling chemical fractionation among the metals Zn and Cd, for (ii) probing the conceivable interaction of all metals with the biological cycle, as well as for (iii) providing the necessary but rare accurate data on such metals, to distinguish between natural occurrence and anthropogenic inputs, i.e., pollution, of these metals in coastal seas.

Both Ni and Cu are known to have biological functions (Da Silva and Williams, 1993). Their vertical distributions in the temperate oceans are akin (Cu) or closely similar (Ni) to those of the major nutrients (Bruland, 1980), further suggesting their involvement in the biological cycle.

Zn and Cd co-exist in mineral rocks, including ore bodies, in an average elemental ratio Zn:Cd of about 600 (Taylor, 1964) to 900 (Chester, 1990).

Within the temperate oceans the vertical profiles of Zn and Cd also exhibit great similarity (Bruland, 1980). Both elements are depleted in surface waters and enriched in deep waters, closely following the distributions of major nutrients silicate and nitrate/phosphate, respectively. This suggests their strong involvement in the biological cycling of the oceans (Broecker and Peng, 1982) but there are some differences. Firstly, Zn is well recognized as a key element in biological functions, notably in the enzyme carbonic anhydrase and in Zn fingers for DNA reproduction (Da Silva and Williams, 1993) while until recently Cd was assumed to have no biological function (Price and Morel, 1990; Da Silva and Williams, 1993). Secondly, Zn is more closely correlated with silicate (or alkalinity) and Cd with phosphate (or nitrate). This might be indicative of a stronger association of Zn with organisms forming hard parts, i.e., opaline diatom frustules or calcareous coccoliths (*Emiliania huxleyi*) and foraminifera shells. Also, the correlations themselves (Zn–Si and $Cd–PO_4$) do somewhat vary, in more or less consistent manner, over the globe (Saager et al., 1992; de Baar et al., 1994; Saager, 1994; Löscher et al., 1997; Yeats, 1998). Thirdly, the elemental ratio Zn:Cd is very low at about 5–10 in the various deep ocean basins as compared to the $\sim$600–900 ratio in the continental crust and deep sea sediments alike.

The metallic element Pb is different from the above Ni, Cu, Zn and Cd in that its natural occurrence in seawater is trivial. In the Northern hemisphere, the natural Pb is virtually negligible compared to the anthropogenic input largely from emissions of gasoline Pb into the atmosphere (Wu and Boyle, 1997). Latter type emissions are now also slowly becoming phased out in Europe; however, some emissions from other industrial activities remain, while some of the inventory of anthropogenic Pb within recent sediments (Nolting and Helder, 1991; van Alsenoy et al., 1993) continues to be released into overlying waters.

In 1993, a research cruise for investigating a bloom of the coccolithophore *E. huxleyi* (Buitenhuis et al., 1996; van der Wal et al., 1996) was providing the opportunity to study trace metals, meanwhile assessing whether such bloom would affect trace metal distributions. Existing literature data generally shows elevated metal concentrations in the North Sea versus the Atlantic Ocean. Plankton blooms may act as a trap for removing metals from the water column, thus maintaining the gradient of metals between North Sea and Atlantic Ocean. Alternatively, an observed dramatic increase of metals Cd and Cu at the shelf edge has been ascribed to intense remineralization in this region (Kremling, 1983, 1985). New data are now presented on Ni, Cu, Zn, Cd and Pb in the scarcely investigated region of the northern North Sea. Parallel investigations of concentrations and speciation of iron, and iron enrichment experiments during the same cruise were reported separately by Gledhill et al. (1998) and Timmermans et al. (1998).

2. Sampling and analysis

Samples were collected during the BLOOM cruise aboard RV *Pelagia* from June 28 until July 14, 1993. The main research area was situated east of the Shetland Islands where a phytoplankton bloom of the coccolithophore *E. huxleyi* was present, roughly between 59 and 61°N. The central sector of the research area was dominated by loose coccoliths of *E. huxleyi*, (Buitenhuis et al., 1996; van der Wal et al., 1996) and will be called the high-reflectance zone.

Table 1
Temperature, salinity and concentrations of copper, cadmium, lead, zinc, nickel and nutrients in the North Sea. Concentrations at 0 m are total dissolvable metal concentrations

Station	Depth (m)	Temp. (°C)	Salinity	Cu (nM)	Cd (pM)	Pb (pM)	Zn (nM)	Ni (nM)	NO_3 (μM)	PO_4 (μM)	Si (μM)
Station 3-2	0			1.82	29	111	3.0	3.5	0.64	0.08	0.40
57.33.36N											
2.21.69E											
Station 5-2	0	12.1	35.2	1.38	12	100	1.9	2.6	0.41	0.08	0.70
59.57.80N	10	11.5	34.6	1.58	29	151	3.5	3.9	0.62	0.07	
1.00.39E	20	10.8	35.7						2.14	0.07	
	30	10.2	35.2	1.40	12	227	10.9	2.5	3.17	0.16	
Station 6-1	0			1.36	3	89	4.0	2.9	0.63	0.08	
60 12.3N	10			1.43	12	129	7.4	4.8	0.36	0.07	
01 00.83E	20			1.73		90	4.2	2.4	0.92	0.09	
	30					67	5.4	6.8	0.74	0.14	
	40			1.41	28	170	8.1	2.8	2.73	0.21	
	50			2.62	49	124	5.4	3.7	4.79	0.48	
Station 7-2	0	12.1	35.2	2.09	75	112	4.7	6.1	0.13	0.05	0.41
60 29.36N	10	11.5	34.6	2.01	38	141	3.3	6.1	0.09	0.04	0.45
01 12.20E	20	10.8	35.7	2.78	50	70	2.5	4.7	0.14	0.04	0.45
	30	10.2	35.2	1.34	13	86	3.3	2.9	0.29	0.12	0.62
	40	8.5	35.3	1.59	14	182	5.0	6.4	0.23	0.08	0.59
	50	7.8	35.3	0.99	36	76	3.2	3.0	1.12	0.30	1.00
Station 7-3	0			2.89	54	165	6.1	3.2	0.17	0.07	0.44
60 29.42N	10			4.34	37	590	16.2	5.4	0.22	0.07	0.42
01 17.23E	20			1.79	5	108	3.2	3.0	0.11	0.07	0.41
	30			1.47	19	111	4.7	2.0	0.28	0.16	0.72
	40			1.08	36	166	4.7	2.9	1.19	0.31	1.07
	50			1.16	42	137	3.0	1.9	3.14	0.45	1.38
Station 8-1	0			1.57	44	75	2.5	3.8	0.19	0.07	0.44
60 38.96N	10			3.90	25	361	12.1	4.5	0.21	0.07	0.44
01 12.89E	20			1.44	39	110	3.2	3.5	0.34	0.08	0.74
	30			1.05	15	58	3.3	3.3	0.81	0.12	0.99
	40			1.57	42	132	5.0	3.5	1.51	0.22	0.85
	50			1.55	23	135	3.9	6.0	2.28	0.31	0.77
Station 9-1	0			1.19	42	67	2.5	3.0	4.89	0.35	1.04
60 58.33N	10			2.81	13	159	4.2	4.3	5.55	0.35	1.03
00 40.33E	20			1.59	1	101	2.8	4.0	4.71	0.38	1.02
	30			1.29	12	68	2.3	3.1	5.56	0.41	1.26
	40			1.63	18	212	4.5	3.9	6.57	0.44	1.36
	50			1.44	20	243	3.0	5.4	6.71	0.51	1.52
Station 10-1	0			1.65	74	79	4.4	4.8	6.77	0.45	1.67
61 42.8N	10			1.40	86	58	4.0	3.3	6.20	0.44	1.68
01 10.3W	20			1.65	110	185	5.7	5.2	6.80	0.48	1.68
	30			1.52	28	69	3.5	3.1	7.20	0.53	1.70
	40			1.68	80	133	4.7	5.0	8.30	0.63	2.38
	50			1.32		107	3.3	2.8	10.68	0.74	3.34
	90			1.25	48	91	4.7	2.8	12.31	0.84	4.49
Station 12-4	0	10.3	35.3	0.81	28	98	1.6	3.2	0.57	0.09	0.30
60 04.39	5	10.3	35.3	1.22	0	54	8.2	3.1	0.51	0.09	0.35
00 09.65E	10	10.3	35.3	1.03	43	115	18.2	4.1	0.79	0.08	0.33
	20	10.3	35.3		54	555	2.6	5.9	0.59	0.06	0.44
	40	9.2	35.3	1.71	7	155	5.0	3.0	1.85	0.23	0.50
	50	8.5	35.3	1.59	240	97	3.0	7.5	5.63	0.54	1.75

Table 1 (continued)

Station	Depth (m)	Temp. (°C)	Salinity	Cu (nM)	Cd (pM)	Pb(pM)	Zn (nM)	Ni (nM)	NO_3 (μM)	PO_4 (μM)	Si (μM)
Station 15-2	0	11.1	34.9	1.84	39	155	6.1	3.9	0.20	0.11	0.52
60 28.3N	10	11.0	34.9	1.98	15	94	4.7	3.6	0.13	0.09	0.49
01 23.2E	20	10.5	35.0	2.03	26	162	5.4	3.7	0.18	0.11	0.54
	30	10.5	35.0	1.35	29	74	3.9	3.2	0.38	0.18	0.64
	40	8.5	35.3	1.47	71	112	5.4	3.0	4.59	0.51	1.80
Station 15-4	0	11.3	34.9	2.36	40	158	16.9	3.2	0.17	0.09	0.43
60 27.46N	10	11.1	34.9	1.77	59	101	6.7	3.0	0.17	0.09	0.45
01 24.91E	20	10.7	34.9	1.66	8	119	4.7	3.2	0.23	0.09	0.48
	30	9.9	35.2	1.29	5	45	4.5	2.8	0.65	0.15	0.60
	35	8.8	35.2	1.40	84	94	4.5	3.2	1.00	0.27	0.78
	40	8.5	35.2	1.99	49	62	4.9	5.7	3.24	0.44	1.00
Station 15-9	50	8.1	35.3	1.57	92	94	4.4	7.7	8.63	0.67	2.59
60 28.99N	70	7.8	35.3	1.40	70	71	4.4	2.8	10.14	0.80	4.04
01 23.24E											
Station 17-2	0	11.2	33.1	3.32	73	232	20.6	4.5	0.07	0.10	0.23
61 00.44N	10	11.2	33.1	3.46	146	102	7.2	8.9	0.06	0.07	0.22
02 59.37E	18	11.1	33.1	3.46	290	123	8.4	3.9	0.05	0.07	0.28
	25	10.8	33.3	1.77	97	81	7.2	7.8	0.11	0.08	0.15
	45	10.2	35.0	1.40	132	54	3.3	2.9	6.01	0.40	1.86
	55	9.6	35.1	1.16	75	47	2.8	3.8	7.62	0.58	2.32
Station 18-2	0	10.7	35.3	1.25	48	72		2.9	6.07	0.42	1.30
61.47.82N	10	10.7	35.3	1.57	22	41	5.5	3.1	6.32	0.42	1.41
1.02.76W	30	10.7	35.3						6.45	0.46	1.42
	90	9.6	35.3	1.45	28	91	3.8	2.8	12.31	0.84	4.49
Station 19-3	0	11.0	35.4	19.40	271	581	50.2	3.0	0.12	0.08	0.32
60 25.32N	10	10.9	35.3	1.66	14	62	3.2	2.4	0.10	0.07	0.35
00 34.32E	20	10.6	35.3	2.15	62	145	6.1	5.9	0.26	0.09	0.36
	30	10.4	35.3	1.92	49	101	5.9	2.8	0.36	0.12	0.41
	50	9.1	35.3	3.04	142	125	5.4	3.0	1.15	0.23	0.57
	70	8.2	35.3	1.81	179	96	3.7	5.3	8.68	0.75	3.28
Station 19-6	0	11.5	35.4	1.57	50	70	5.0	3.0	3.60	0.24	0.71
60 31.72N	10	10.8	35.3						3.45	0.22	0.68
00 23.35E	20	10.7	35.3	2.15		170	5.7	2.3	3.52	0.22	0.72
	30	10.5	35.3	1.44	39	72	3.1	2.4	4.54	0.31	0.89
	50	9.3	35.3	1.77	5	38	2.8	2.8	7.14	0.57	2.36
	70	8.6	35.3	1.66	61	93	3.1	2.4	8.88	0.72	3.37
Station 33-2	0	10.9	35.2	1.55	10	73	2.4	2.2	0.08	0.08	0.75
59 36.87N	10	10.9	35.1	1.54	88	42	4.7	2.3	0.14	0.09	0.79
00 06.97E	20	10.9	35.1	1.10	39	34	2.4	2.2	0.09	0.09	0.79
	30	10.8	35.1	1.61	44	104	7.0	2.2	0.14	0.09	0.83
	50	6.8	35.2	1.57	193	40	5.1	2.4	9.91	0.78	4.26
	70	6.5	35.2	1.80	102	138	4.5	2.6	11.18	0.88	4.91
Station 34-1	0			1.65	103	39	2.2	3.3	0.04	0.11	0.20
56 30.22N	10			1.91	149	47	5.2	3.7	0.02	0.09	0.23
00 50.11W	20			2.25	57	125	8.8	4.6	0.03	0.07	0.25
	30			2.22	52	71	4.5	3.2	0.20	0.09	0.22
	50			2.79	95	158	7.2	3.6	1.84	0.48	2.34
	70			2.17	294	116	4.9	3.4	1.86	0.46	2.43

The sampling strategy was mainly dictated by the biological objectives.

For trace metal work, a class 100 clean air container was installed on board ship. All equipment used was thoroughly cleaned with acids in the home laboratory and stored in plastic bags. A rubber raft, holding a small teflon-coated winch with kevlar wire, 1.7 l Go-Flo water samplers and messengers made of

teflon, was used for sampling. Contamination by the ship was avoided by sampling at least 500 m up-wind from the research vessel (Nolting and De Jong, 1994). Stations with cast numbers and positions are given in Fig. 1 and Table 1. Stations 7-2, 7-3, 15-2, 15-4, 15-9, 19-3 and 19-6 were drifting stations and lasted 24 h. At these positions, a morning and an afternoon cast was deployed, indicated by different cast numbers. Station 19 was situated at the edge of the active bloom, and at this station the two casts were chosen in such a way that 19-3 was just inside and 19-6 just outside the bloom. The other stations were sampled while sailing through the research area. At least six depths were sampled in the upper 90-m water column and the very surface layer. The latter sample was taken by filling a bottle directly from the bow of the slowly moving raft, wearing plastic gloves. At stations 15-4 and 15-9, two different casts were combined to obtain one profile. Samples at depth were collected with the Go-Flo samplers attached to the kevlar line of the small winch and lowered by hand. At depth, the samplers were closed by releasing the messengers. After recovery, the samplers were directly wrapped in plastic bags, transported to the ship and brought into the clean air container. There the plastic bags were removed from the samplers and the water was directly in-line filtered, under 1 atm nitrogen pressure over 0.4 μm pre-cleaned Nuclepore filters, using teflon filter holders. The samples were then acidified with three times sub-boiled quartz distilled HNO_3 to pH 2. Surface samples were not filtered but directly acidified with HNO_3 to pH 2, and represent total dissolvable concentrations. Several days after collection of the samples, trace metals were extracted from solution with an APDC/DDDC freon extraction method in teflon separatory funnels, and back-extracted with HNO_3 in 30-ml teflon vials (Danielsson et al., 1978, 1982). These vials were wrapped in plastic bags and stored in a refrigerator at 4°C until analysis. Cu, Cd and Pb were determined with a Perkin Elmer 5100 Zeeman Graphite Furnace Atomic Absorption Spectrophotometer (G.F.A.A.S.), using the Stabilised Temperature Platform Furnace (S.T.P.F.). Ni was determined with wall atomisation and Zn by flame A.A.S. Standards with the same acid concentration were used for calibration. The recoveries were verified with standard additions to samples which were run during the analysis (Nolting and De Jong, 1994), and was between 90 and 100% for all studied elements. Reported values have been corrected for this efficiency. Six blanks of previously three times extracted sea water, to which, subsequently, the standard volumes of the used chemicals were added, were run during the whole procedure. This gives the method blanks averaging at 0.10 ± 0.04 nM Cu, 31 ± 4 pM Cd, 7 ± 3 pM Pb, 0.2 ± 0.1 nM Ni and 0.9 ± 0.3 nM Zn. Blank values were subtracted from the obtained values for each element, respectively. With the same procedure, we successfully participated in the certification of a reference seawater (Quevauviller et al., 1992). We are aware of the fact that the Cd blank was rather high taking into account the low Cd value in some samples. So, these low values have to be taken with some caution. Normally, we have much lower blanks (Nolting and De Jong, 1994), but due to unknown reasons the blanks were this time higher. The reproducibility for six replicates was between 2.2% and 6.2% for all metals (Nolting and De Jong, 1994). Nutrients were determined on shipboard using Traacs 800 Auto Analysers (Grasshoff, 1983). Detection limits were 0.02 μM phosphate, 0.02 μM nitrate and 0.10 μM silicate. Salinity and temperature were measured with a Sea-Bird Electronics CTD, type SBE 9 + .

3. Results

3.1. Hydrography

The research area could be divided into three different parts. The northernmost part was characterized by Atlantic waters with high nutrient concentrations (stations 9-1, 10-1, 18-2 and 19-6). An intermediate part comprises the high reflectance zone (stations 5-2, 6-1, 7-2, 7-3, 8-1, 12-4, 15-2, 15-4-9 and 19-3) and finally there is a southern part (outside the bloom and below 60°N) belonging to the central North Sea (stations 3-2, 33-2 and 34-1). Station 17-2 in the Norwegian Trench is added as a reference station.

The research area was characterized by a well mixed surface layer of 20–30 m with a temperature of around 10.5°C, a salinity of 35.3 and low nutrient concentrations (Table 1). For stations 3-2, 6-1, 7-3,

8-1, 9-1, 10-1 and 34-1 no salinity and temperature data are available due to malfunctioning of the CTD Rosette Sampler. These stations could only be characterized by their nutrient concentrations. Some representative profiles of nitrate, phosphate and silicate for the whole research area are given in Fig. 2. Within the high reflectance zone, these profiles show a considerable similarity, with the lowest concentrations in the mixed layer and below this depth increasing to higher values, representing North Atlantic water. Stations 9-1, 10-1 (Fig. 2), 18-2 and 19-6 located north of the bloom show nutrient concentrations similar to those reported by Martin et al. (1993) and Kremling and Pohl (1989) for North-East

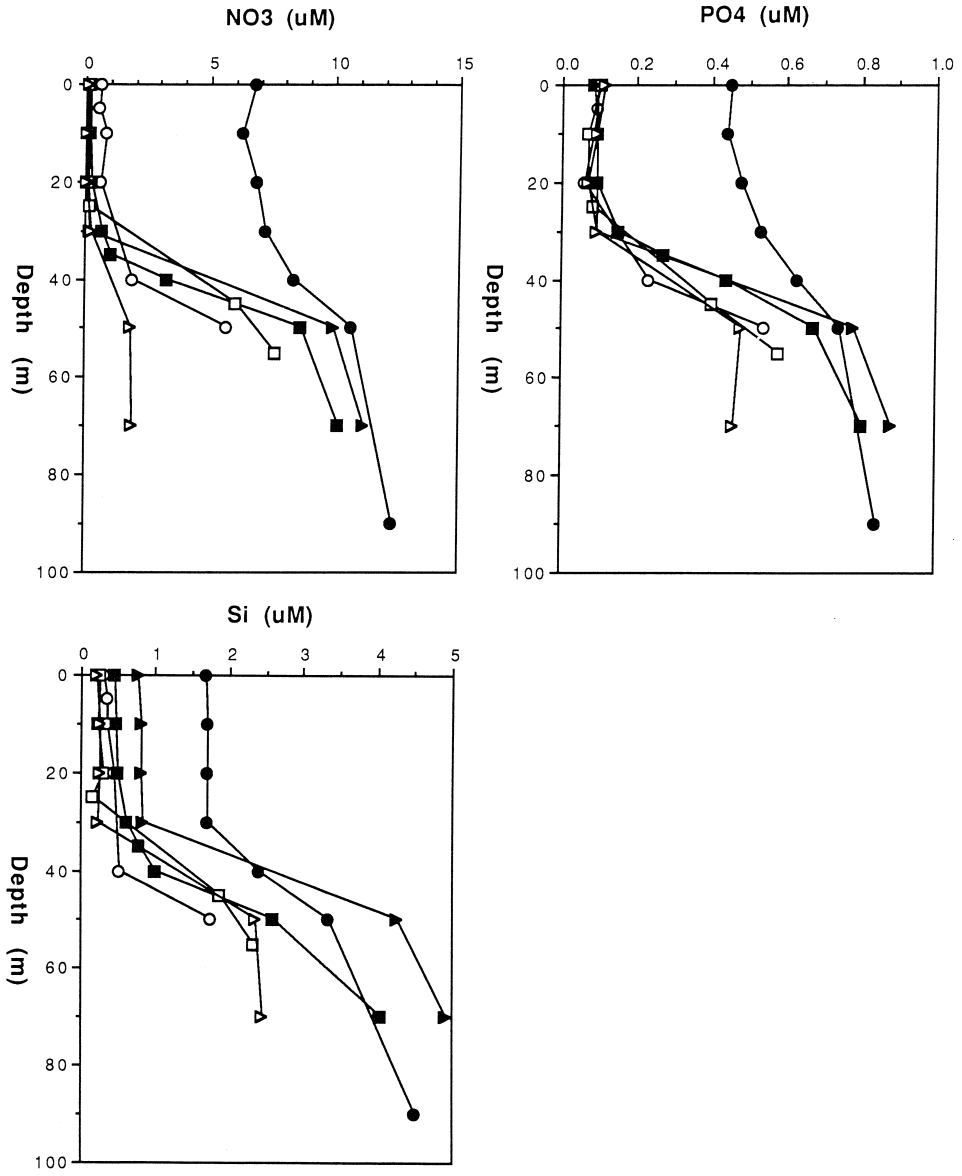

Fig. 2. Depth profiles of dissolved nitrate, phosphate and silicate (μM) at stations 10-1 (●), 12-4 (○), 15-4 (■), 17-2 (□), 33-2 (▲) and 34-1 (△).

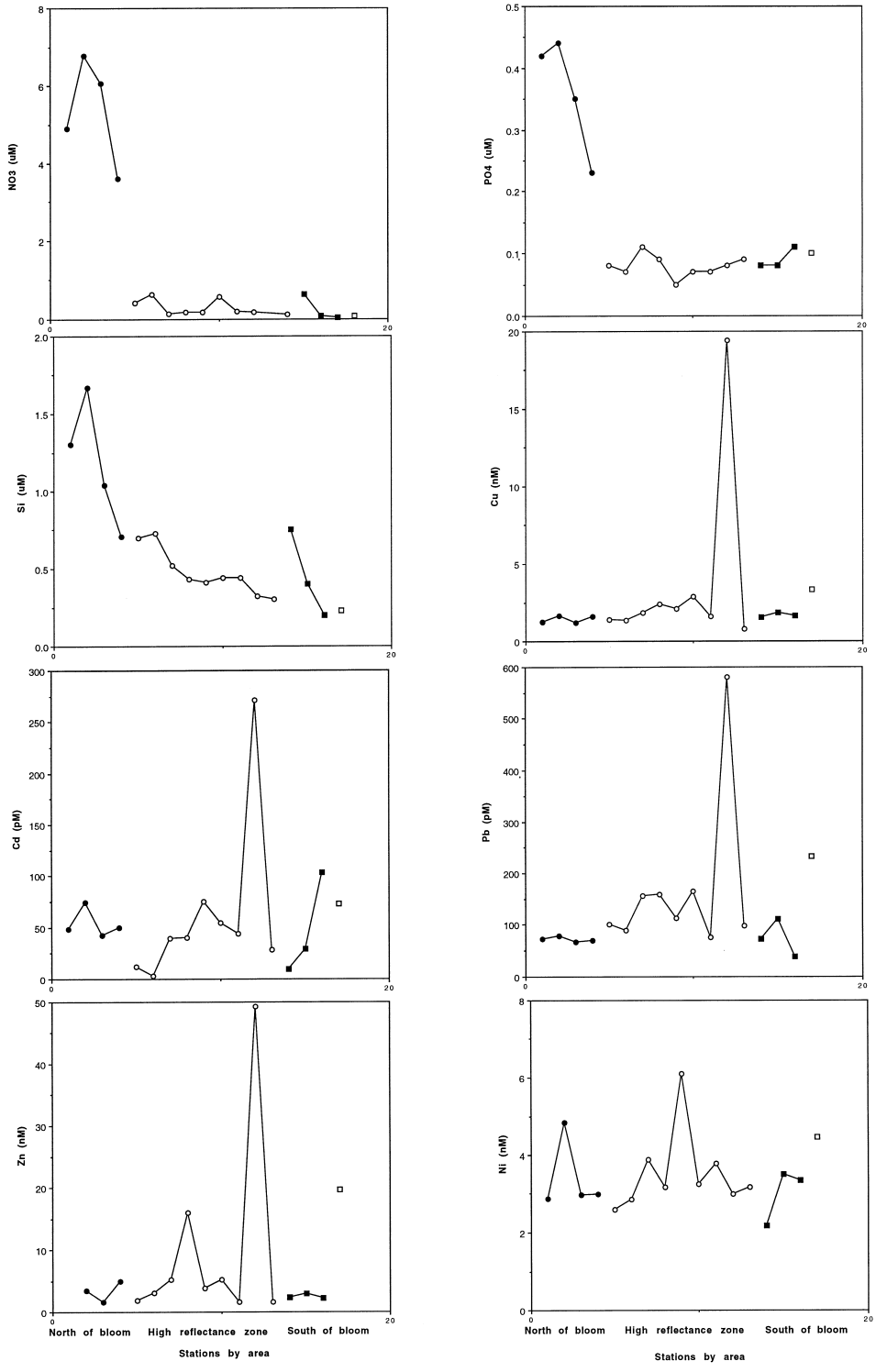
NO3 (uM)
PO4 (uM)
Si (uM)
Cu (nM)
Cd (pM)
Pb (pM)
Zn (nM)
Ni (nM)
North of bloom
High reflectance zone
South of bloom
Stations by area

Table 2
Average (±SD) surface concentrations in the three different areas in the North Sea

	Cu (nM)	Cd (pM)	Pb (pM)	Ni (nM)	Zn (nM)
Atlantic section	$n = 4$	$n = 4$	$n = 4$	$n = 4$	$n = 3$
	1.42 ± 0.23	54 ± 14	72 ± 5	3.41 ± 0.94	$4.0 + 1.3$
Bloom	$n = 8$	$n = 8$	$n = 8$	$n = 8$	$n = 7$
	1.78 ± 0.65	37 ± 23	119 ± 35	3.53 ± 1.05	3.2 ± 1.8
South Bloom	$n = 3$	$n = 3$	$n = 3$	$n = 3$	$n = 3$
	1.67 ± 0.14	47 ± 49	74 ± 36	3.14 ± 1.35	2.5 ± 0.4
Station 17-2	3.32	73	232	4.45	20.6

Atlantic surface waters. Baltic water is indicated in the surface layer at stations 15-2, 15-4-9 and 17-2 by higher temperature and lower salinity (Table 1). Below this surface layer Atlantic water is again clearly identified by the higher nutrient concentrations. The nutrient profile of station 34-1 (Fig. 2) is an indication that we are dealing with central North Sea water, with lower concentrations of silicate, phosphate and nitrate.

3.2. Distributions in unfiltered surface waters

The results of the horizontal distribution, sorted by region, of the nutrients, NO_3, PO_4 and Si and the trace elements Ni, Cu, Zn, Cd and Pb (total dissolvable in unfiltered seawater) are presented in Fig. 3 and included in Table 1. The nutrient distribution reflects the pattern already described in Section 3.1, high values north of the high reflectance zone fast decreasing to lower concentrations in the other areas. However, this decrease was not reflected in the trace metal distributions (Fig. 3).

Concentrations of total dissolvable Ni did not fluctuate much and the overall mean is 3.50 ± 0.96 nM including all data points (Table 2). Despite the fact that Ni shows a nutrient-like vertical distribution in the open oceans (Bruland, 1980; Saager et al., 1992; Saager et al., 1997), it appears that its concentration in oceanic surface waters is not depleted and more or less uniform around 3 nM (Bruland, 1980; Kremling and Pohl, 1989; Saager et al., 1992; Martin et al., 1993; Saager et al., 1997). Our unfiltered Ni concentrations are also in very good agreement with the filtered values given by Kremling and Hydes (1988) at 3.5 ± 0.9 nM.

Total dissolvable Cu concentrations ranged between 0.81 and 3.32 nM with an overall mean of 1.77 ± 0.64 nM ($n = 16$). At station 19-3, a very high concentration of 19.4 nM was found. At the same station, all other metals excluding Ni but including iron (Gledhill et al., 1998, two independently collected samples), showed similar very high values. For statistical reasons the values at this station, although realistic, were deemed to be outliers and are not used for average calculations for the studied metals. Average concentrations for each specific region are given in Table 2 and show no significant difference, although the lowest concentrations were found in the northern area. Despite the fact that our very surface water samples were not filtered, the Cu concentrations were similar to those reported previously for filtered samples by Kremling and Hydes (1988) and almost identical with filtered values reported by Danielsson and Westerlund (1983) and Pohl et al. (1993), for Arctic Atlantic waters. This can be an indication that anthropogenic inputs of Cu are not significant in these northern North Sea waters, this in contrast to the southern North Sea where elevated Cu concentrations have been found (Nolting, 1986; Tappin et al., 1995).

Fig. 3. Surface distributions of nitrate, phosphate, silicate (μM), copper (nM), cadmium (pM), lead (pM), zinc (nM) and nickel (nM) presented by area. Stations are presented in following order: {18-2, 10-1, 9-1, 19-6} {5-2, 6-1, 15-2, 15-4, 7-2, 7-3, 8-1, 19-3, 12-4} {33-2, 3-2, 34-1} {17-2}.

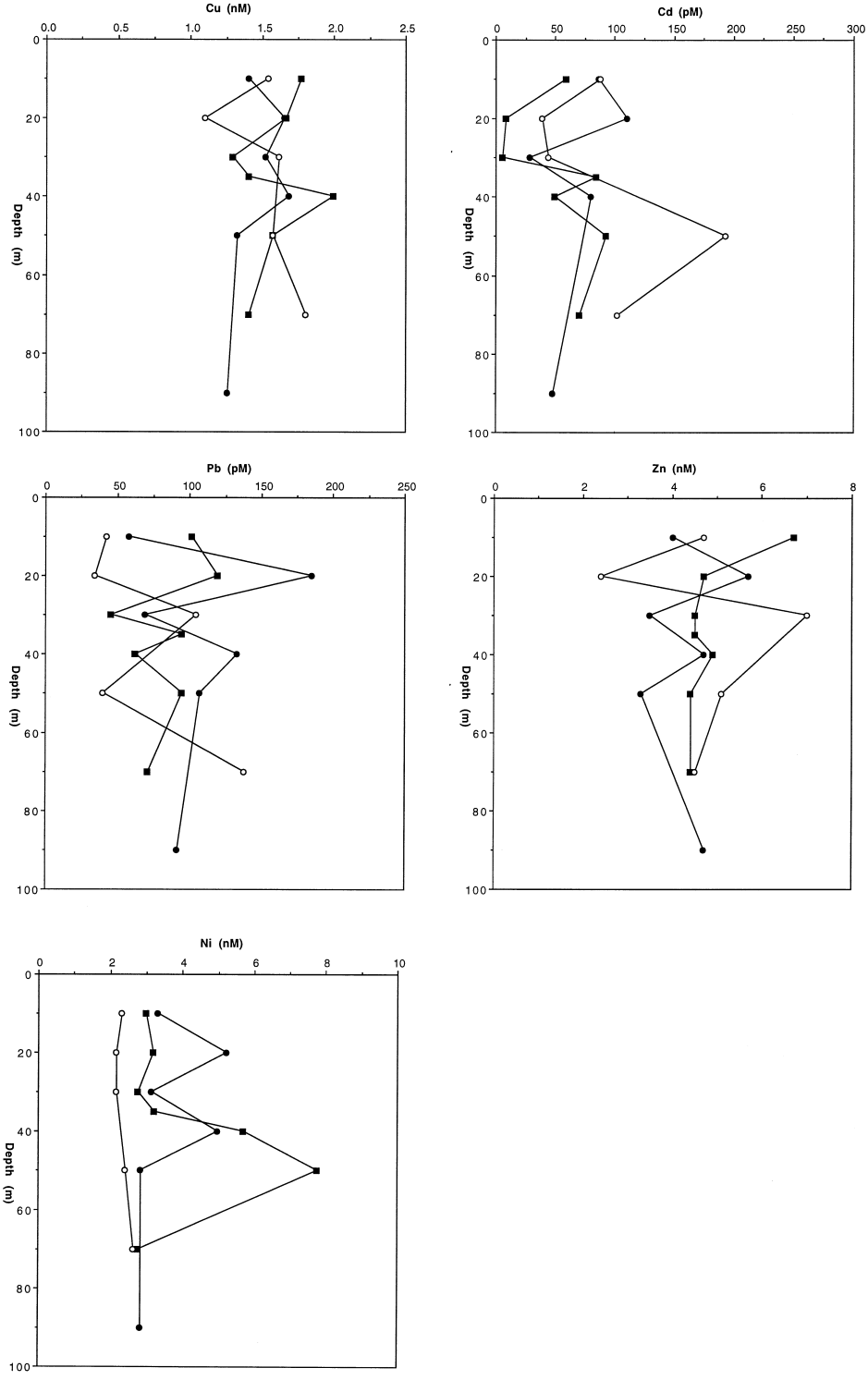
Cu (nM)
0.0 0.5 1.0 1.5 2.0 2.5
Cd (pM)
0 50 100 150 200 250 300
Pb (pM)
0 50 100 150 200 250
Zn (nM)
0 2 4 6 8
Ni (nM)
0 2 4 6 8 10
Depth (m)
0 20 40 60 80 100

Table 3
Average (±SD) dissolved trace metal concentrations in the upper water layer in the three different areas

	Cu (nM)	Cd (pM)	Pb (pM)	Ni (nM)	Zn (nM)
Atlantic section	$n = 17$	$n = 15$	$n = 17$	$n = 17$	$n = 17$
	1.62 ± 0.38	38 ± 33	114 ± 61	3.45 ± 1.00	3.9 ± 1.1
Bloom	$n = 42$	$n = 40$	$n = 43$	$n = 43$	$n = 43$
	1.75 ± 0.69	47 ± 47	135 ± 113	3.96 ± 1.53	5.5 ± 3.3
South Bloom	$n = 10$	$n = 10$	$n = 10$	$n = 10$	$n = 10$
	1.90 ± 0.48	111 ± 81	88 ± 46	3.02 ± 0.81	5.4 ± 1.8

Total dissolvable Zn concentrations ranged from 1.6 to 5.2 nM with exception of the higher values found at stations 19-3 and 17-2 and the 16.9 nM at station 15-4. Very few Zn data are published for the northern North Sea, possibly because of sampling difficulties and contamination problems. Fileman et al. (1991) reported Zn concentrations in filtered surface waters over the Dogger Bank, which ranged between 2.44 and 9.33 nM (average 3.9 nM). This is in very good agreement with the mean Zn concentration of 3.1 nM detected during our study. Duinker and Nolting (1982) and Nolting (1986) reported Zn concentrations in surface waters of the Southern Bight, with very high values in the coastal areas, decreasing seaward to concentrations similar to those observed in this study. Trace metal results, comprising annual surveys in the English Channel and the central- and southern North Sea, were recently presented by Tappin et al. (1993; 1995). They reported Zn values for the central North Sea, between 3 and 6 nM, which is in the same range as found in this study.

Total dissolvable Cd ranged between 3 and 103 pM (Fig. 3) with an overall mean of 45 ± 27 pM ($n = 16$) which is a factor of two lower than values reported by Kremling and Hydes (1988). Lowest Cd concentrations (~ 10 pM) were found south of the bloom in the central North Sea. The Zn:Cd ratio of the unfiltered surface waters had an average value of 213 ± 316 ($n = 13$) and will be further discussed below.

The overall mean concentration of Pb (range 39–232 pM) is 106 ± 49 pM, and is a factor of three lower than values reported by Brügmann et al. (1985) for the same research area. Pb values reported for the north Atlantic by Brügmann et al. (1985) and Martin et al. (1993) agree very well with the ones found at our northern stations.

The higher metal values found in unfiltered surface samples at station 19-3 could be caused by an increased particle concentration, either organic or inorganic.

Overall, the concentrations of total dissolvable Ni, Cu, Zn, Cd and Pb are exhibiting a similar distribution pattern, with only small variations between the different regions.

3.3. Vertical distributions in filtered waters

Examples of depth profiles of Ni, Cu, Zn and Cd, as well as Pb are given in Fig. 4 specific for each region, that is for the Atlantic section station 10-1, the high reflectance zone station 15-4, and for the central North Sea station 33. All other data can been found in Table 1. The mean concentrations (±1 SD) of all dissolved trace elements in the three different regions are given in Table 3.

The mean Ni concentration of 3.66 ± 1.36 nM in the upper water column of the northern North Sea (Fig. 4) is in very good agreement with the findings of Kremling et al. (1987) and of Tappin et al. (1995) for the central North Sea and almost identical to concentrations found at 59°N, 20°W in the Atlantic Ocean (Martin et al., 1993). This is in agreement with the observations of Burton et al. (1993) who

Fig. 4. Depth profiles of dissolved copper (nM), cadmium (pM), lead (pM), zinc (nM) and nickel (nM) at stations 10-1 (●), 15-4 (■), and 33-2 (○).

suggested the strong conservative behaviour of Ni in the North Sea waters. This is also suggested from the ratio of deep water concentration against surface concentration for Atlantic waters (Martin et al., 1993) which is for Zn 6, for Cu 1.5, for Cd 4 and 1 for Ni.

The concentration of Cu was found to be around 1.61 nM below 20 m at all stations (Fig. 4). This is about 0.5 nM higher than the 1.1 nM Cu values observed in the north Atlantic (59°N, 20°W) by Martin et al. (1993), but 0.5 nM lower than those given by Cossa et al. (1992) for an Atlantic station (46°N, 6°W). The mean Cu concentrations increase from north to south, although the differences between the three areas were small (Table 3). Depth profiles of Cu south of our research area, given by Kremling et al. (1987), show higher concentrations of around 3 nM and are comparable with those reported recently by Tappin et al. (1995).

With the exception of some higher sub-surface values, the mean Zn concentration in the study area was 4.5 ± 1.6 nM, ($n = 79$). The lowest mean Zn concentration of 3.9 nM was found in the northern part of the North Sea (Fig. 4), those in the other two areas are equal and somewhat higher (Table 3). Very few dissolved Zn profiles are published for the northern North Sea. Danielsson et al. (1985) published two profiles for this area and their mean Zn value of 5.3 ± 2.6 nM is a little higher than our results. This implies that a value of around 5 nM Zn in the northern North Sea is a very realistic one; however, it is still a factor of 10 higher than the values reported for north Atlantic surface waters (Martin et al., 1993). Nevertheless, the Zn values reported here belong to the lowest ones ever reported for the North Sea. Tappin et al. (1995) found high dissolved Zn concentrations in the southern North Sea and observed a clear seasonality in Zn concentrations, with remarkably higher concentrations in spring than in autumn.

Mean Cd concentrations are almost similar in the high reflectance zone and north of it, while the concentration is clearly higher (> 100 pM) south of the bloom (Table 3). These concentrations belong to the lowest ones reported for this area, and are comparable to those found in oligotrophic surface waters of the north Atlantic (Boyle et al., 1981; Bruland, 1983; Martin et al., 1993; Saager et al., 1997). Kremling et al. (1987) measured Cd concentrations as low as 0.1 nM for a transect south of our research area. The biological cycling of Cd as indicated by a strong correlation with phosphate in the stratified ocean (Boyle, 1988; Frew and Hunter, 1992; Saager and de Baar, 1993; de Baar et al., 1994) is hardly discernible in coastal and shelf seas. The Zn:Cd ratio of the filtered seawater had an average value of 169 ± 141 ($n = 14$) in the Atlantic section stations, 222 ± 236 ($n = 40$) in the high reflectance zone stations, and 71 ± 52 ($n = 10$) in the central North Sea stations. This and the overall Zn:Cd ratio of 186 ± 212 ($n = 64$) will be further discussed below.

There are very few consistent dissolved Pb data for the North Sea available. Generally, the mean concentration of 108 ± 45 pM Pb is a factor of two lower than the values reported by Tappin et al. (1995) for the southern and middle part of the North Sea. Brügmann et al. (1985) and Dicke et al. (1987) were among the first to present reliable Pb profiles for the North Sea. The different distribution pattern of Pb compared to that of the bioactive metals Cu and Cd is indicated by the calculated mean values for each area (Table 3). Where Cu and Cd have their highest concentrations in the southern part of the research area, the highest mean Pb value was found in the high reflectance zone.

Summarizing, despite the strong seasonal stratification, neither significant concentration gradients across the thermocline nor large differences between the three areas could be detected for any element studied.

4. Discussion

4.1. Are there relationships between trace metals and the bloom?

Part of this research was to investigate if, besides the major nutrients, trace element concentrations might be influenced by the coccolithophorid bloom. From the vertical profiles (Fig. 2), it can be seen that nitrate is almost completely utilized in the first 25 m of the well mixed upper layer within the bloom. Outside the bloom higher levels of nitrate were present within the surface waters. Therefore, the cells present in the decaying *E. huxleyi* bloom ap-

peared to be nitrogen limited (van der Wal et al., 1996) and this may have been the prime cause for the decline of the bloom.

In the surface waters, the values for total dissolvable metals represent the complete inventory of dissolved and particulate standing stocks. Within the bloom one might expect some export by settling of particles into deeper waters to lead to a decrease in the overall inventory. However, both inside and outside the bloom, the total trace metal concentrations

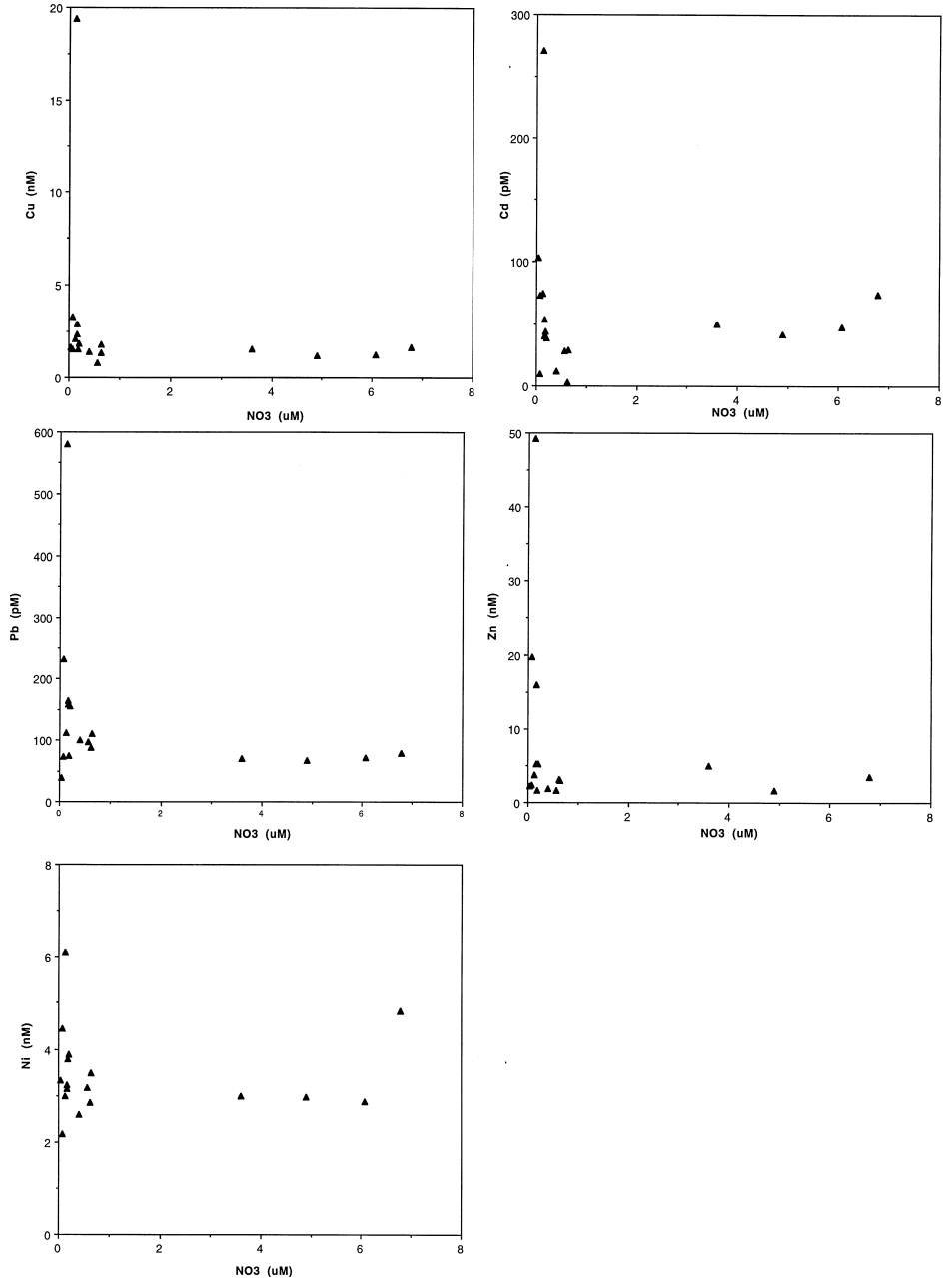

Fig. 5. Correlation between nitrate (μM) and unfiltered copper (nM), cadmium (pM), lead (pM), zinc (nM) and nickel (nM) surface data collected in the northern North Sea.

are almost equal. As a result there is no relationship found with the depletion of nitrate within the blooms (Fig. 5). In fact somewhat higher metal concentrations were found at near-zero nitrate within the bloom where the highest plankton biomass was observed (van der Wal et al., 1996).

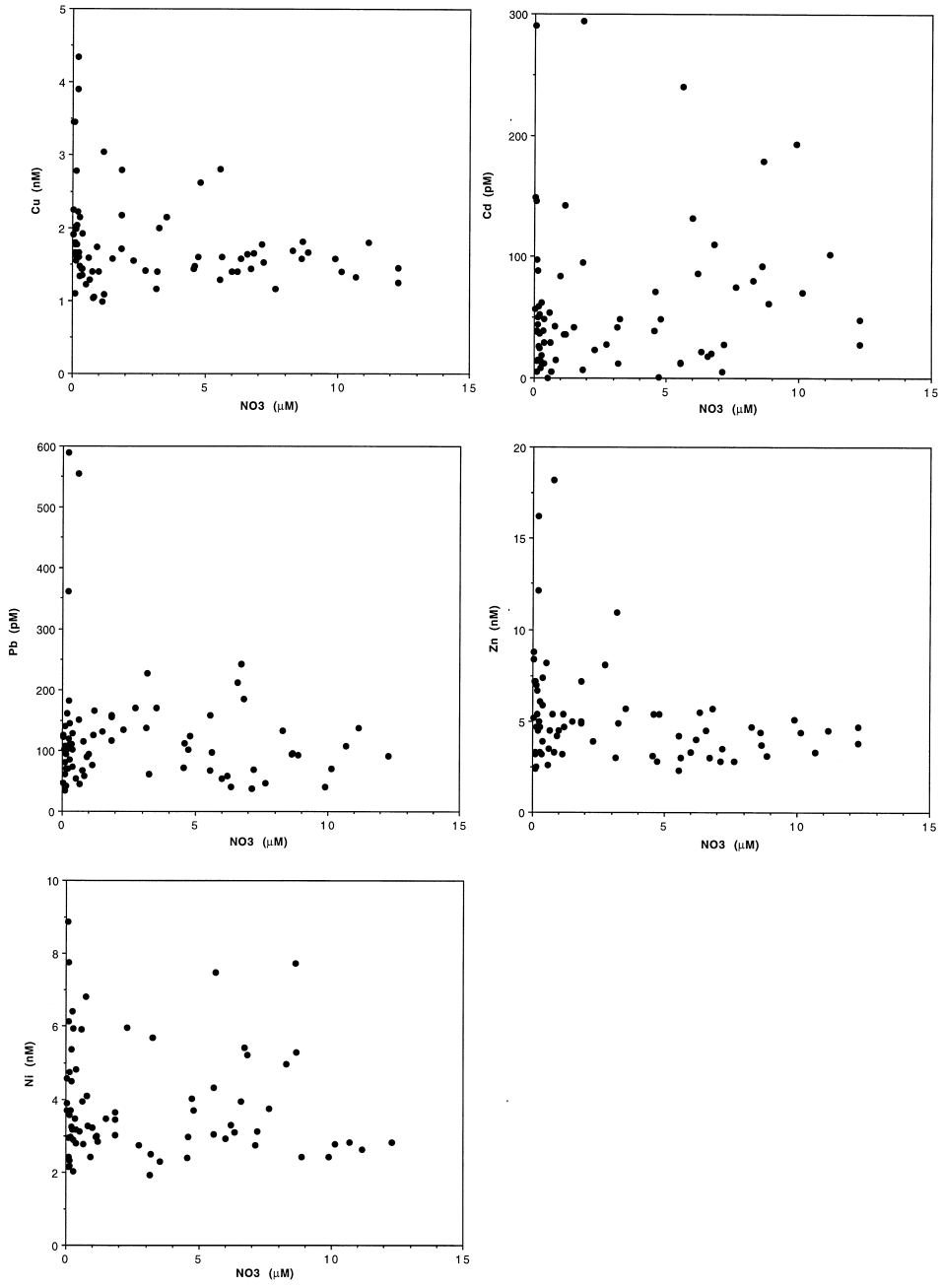

Fig. 6. Correlation between nitrate (μM) and dissolved copper (nM), cadmium (pM), lead (pM), zinc (nM) and nickel (nM) data collected in the northern North Sea.

In Fig. 6, the dissolved sub-surface values of all metals are plotted against nitrate. This shows that at nitrate concentrations higher than 5 μM, resembling Atlantic water, the concentrations of Cu, Zn and Pb are more or less constant. Only at lower nitrate concentrations, comprising different water masses, there is more variation. Here, Cd appears to be the only element that shows some relation with the nutrients, with lowest concentrations at almost zero nitrate. In general, however, the concentration gradients are small for all studied metals in our research area. This confirms the observations of Kremling et al. (1987) and that which was postulated by Burton et al. (1993) for their results in the southern part of the North Sea, ''Although Cd and Zn and, to a lesser extent, Ni and Cu, develop nutrient-like profiles in the water column of the stratified ocean, the coupling of their cycles to the utilization and regeneration of nutrients in the North Sea is not detectable''.

North Sea waters are dominated by a strong exchange with the upper 200–400 m waters of the North Atlantic Ocean, and only in summer a seasonal stratification occurs. This does permit a bloom to develop, which may exhaust one (here nitrate) or another major nutrient, but on its own is not capable of removing all metals as well. For Ni, this is not different from the oceanic situation; as in ocean surface waters, Ni does not become exhausted either. Cd on the other hand does show some depletion within the North Sea bloom akin to its general depletion elsewhere in the surface ocean. Zinc has a much higher abundance, both absolute and relative (see below) in the North Sea than in the open ocean, and the single bloom of *E. huxleyi* is not capable of removing a significant portion of the dissolved Zn. Finally, Pb is deemed particle reactive in the time frame of oceanic processes, but at shorter time scales of mixing and biology in the North Sea this is not evident. Also, due to its transient input from anthropogenic sources a straightforward relation with nutrients is not expected either in the ocean or in the North Sea.

4.2. Fractionations of Zn and Cd

The elemental Zn:Cd ratios here observed are ranging from about 13 to about 1333 and averaging at 186 ± 212 for the dissolved (filtered) seawater samples, as compared to 213 ± 316 for the unfiltered surface water samples. These ratio values are in between, on the one hand, the abundance ratio of about 600–900 in continental source rocks (Taylor, 1964; Chester, 1990), and on the other hand, the values of 5–10 in oceanic waters, with lowest ratio at about 5 in the North Atlantic Ocean adjacent to the North Sea study area (Martin et al., 1993). Apparently, the coastal North Sea is a mixing region of continental inputs with high Zn:Cd and oceanic waters with low Zn:Cd ratios.

This appears consistent with observations of the ratio Zn:Cd in the river Scheldt contributing to the North Sea, as well as in other rivers worldwide. The dissolved Zn (40 to 380 nM) and Cd (0.5 to 5 nM) observed in 1978 in the Scheldt by Duinker et al. (1982) correspond to ratios varying from 38 to 308 with an average of 118 ± 71 for $n = 84$ samples. These concentrations are quite high compared to values in the Mississippi river (Shiller, 1997) and the pristine Amazone river (Boyle et al., 1982; Shiller and Boyle, 1985). Nevertheless, the elemental ratio Zn:Cd in the lower Mississippi river (discharge weighted means in various years) is similar at 29 (1991–1992), 36 (1992–1993) and 25 (1982–1984), respectively (Shiller, 1997). The dissolved Zn and Cd in the Gironde river have higher dissolved concentrations but again the elemental ratio Zn:Cd is similar at about 40–60 (Kraepiel et al., 1997). The particulate Zn:Cd is higher at 95–500 in the river endmember, and quite uniformly near crustal abundance at about 800 throughout the estuary (Kraepiel et al., 1997).

Apparently, the oceans maintain an about hundredfold fractionation of Zn and Cd. The metals Zn and Cd are weathered in a high crustal ratio of about 600–900 (Taylor, 1964; Chester, 1990), then exist in ocean waters at a low ratio 5–10 but eventually are removed again in marine sediments at the high ratio of about 900 (Chester, 1990). This is akin to the well known fractionations among the Rare Earth Elements between the crustal source, oceanic water column and sedimentary sink (de Baar et al., 1985). For Zn and Cd, we reckon a fractionation factor of about 100 to be accounted for.

4.2.1. Inorganic fractionation

The prime mechanism for the two orders of magnitude Cd enrichment of oceanic waters may well be

the complexation of Cd by chloride anions, which is about 1000-fold stronger than chloride complexation of Zn (Cotton and Wilkinson, 1980). Consequently, Cd is predicted to be only about 3% in the free ionic form in seawater, as compared to about 64% free Zn-ion (Byrne et al., 1988). The predicted free ionic state or activity has often been understood to be indicative for the reactivity of a metal ion to other moieties, that is to uptake into plankton cells as well as to adsorption on the outer surface of suspended particles, of which some portion is settling into the deep sea towards the sediments. Thus, a high percentage free ion would lead to a short residence time in the oceans, and from the inorganic speciation alone a 21-fold longer residence time of Cd versus Zn would be expected, as compared to the observed factor of about 100. This chloride complexation difference is not only straightforward but also operative throughout the world oceans.

In each individual estuary and coastal sea there is quite some natural variability due to similar variation of crustal input sources. Nevertheless, both our observations in the North Sea and the various findings in rivers and estuaries fall in between the low oceanic ratio (5–10) and the high crustal ratio 600–900. It is noticed that the rivers and estuaries have generally a lower dissolved ratio 25–100 as compared to the average Zn:Cd at 194 in filtered seawater at our North Sea stations. For simple mixing between continental endmembers (600–900) and an oceanic endmember (5–10) one would instead expect the rivers and estuaries to exhibit a higher ratio than the North Sea. Obviously, the ratio Zn:Cd of 68 ± 62 ($n = 69$) reported by Tappin et al. (1995) for the southern and central North Sea is in very good agreement with our value of 71 ± 52 ($n = 10$) for the central North Sea and values of 70–90 found by Zwolsman et al. (1997) in the more saline part of the river Scheldt. On the other hand, the North Sea dissolved values of Fileman et al. (1991) average at Zn:Cd = 26 largely due to the higher Cd values at their more southern and shallower (< 50 m) Doggersbank side. One extra factor here is the additional role of sulfide precipitation within various estuaries as discussed elsewhere (Nolting et al., 1999). Sulfides also play a role in shallow coastal sediments, e.g., the Doggersbank, and would become less significant towards the deep open ocean. Moreover, in rivers and estuaries at lower chloride, i.e., salinity, the inorganic complexation becomes dominated by other hydrolyzed and carbonate species, such that at adequate oxygenation and higher pH the Zn is more complexed than the Cd, as opposed to oceanic waters (Turner et al., 1981).

4.2.2. Organic fractionations

Apart from inorganic speciation and sulfide formation there is the binding to organic moieties to be taken into account. For a given metal, the complexation to dissolved organic ligands would tend to lower its free ionic concentration, hence, make it less reactive to plankton and other particles, i.e., lead to a longer oceanic residence time. On the other hand, a strong affinity to dissolved organic ligand usually also implies a strong affinity to particulate organic ligands on the surfaces of plankton and other particles. The latter mechanism would tend to enhance removal from the oceans, i.e., shorten the residence time. In oceanic surface waters, both dissolved Zn and Cd are strongly complexed by dissolved organic ligands. About 98% of dissolved Zn is in the organic form, the remaining consisting of about 1.1% inorganic complexes and only 0.9% free Zn^{2+} ion (Bruland, 1989). At greater depths (500–600 m), it appears that the organic percentage is decreasing to only about 30% such that quite some free Zn-ion may exist, likely approaching the 64% free as in the above strictly inorganic complexation. The organic complexation of Cd appears to be dominant in the upper 200 m only (Bruland, 1992) such that the percentage free Cd-ion ranges from 0.8% in the upper waters to about 3% in the deep ocean, the latter dominated by inorganic complexes only. Combining both studies of Zn and Cd, it appears that the fractionation factor of about 21 due to inorganic complexation remains valid for the deep oceans. In the surface waters, the fractionation factor includes organic complexation and would become smaller at about 1 due to the similar percentage of free ion for both Zn and Cd. The affinity (stability constants) for organic ligands is similar for both metals, but the Zn-binding ligand appears to be about 10-fold more abundant than the Cd-binding ligand (Bruland, 1989, 1992). Similarly, the removal by adsorption on plankton and other particles is also a matter of relative affinities and particulate ligand concentra-

tions, where inorganic surface sites may also play a role (Byrne and Kim, 1991). Lacking direct observation on this for Zn versus Cd, we will for the time being simply ignore the conceivable fractionation due to either dissolved organic ligands or particulate and inorganic surface sites.

4.2.3. Biological fractionation

The about 100-fold fractionation in the oceans is largely accounted for by the 21-fold stronger inorganic complexation of Cd. The remaining factor of about 5 might well be ascribed to preferential biological uptake of Zn. Briefly, Zn is, after Fe, the second most important essential metal. Until recently, it was assumed that Cd had no biological function at all, its strong correlation with the nutrients phosphate and nitrate presumably being more or less fortuitous due to adsorptive scavenging removal with biogenic particles. With Zn being so intrinsically involved in the biological cycle it is expected to have a shorter oceanic residence time, eventually due to its more efficient burial along with organic remains, as also suggested by the ultimately high Zn:Cd ratio of about 900 in marine sediments (Chester, 1990). Recently, it was shown that Cd, as well as Co, may substitute for Zn in growth of various phytoplankton species including *E. huxleyi* (Price and Morel, 1990; Lee and Morel, 1995; Lee et al., 1995; Sunda and Huntsman, 1997) with special emphasis on carbonic anhydrase and its role in alleviating CO_2-limitation. From this, and the natural low Zn:Cd ratio in oceanic waters, and the very close correlation of Cd with phosphate in the global ocean, one may well hypothesize that Cd has true natural functions in carbonic anhydrase and elsewhere in marine plankton, rather than just being a substitute for Zn. Nevertheless, Zn having so many biochemical functions it remains most likely that preferential uptake of Zn is taking place, and some fivefold faster biological removal of Zn is deemed quite reasonable.

4.3. Natural abundances and pollution sources

The observed distributions of Ni, Cu and Cd in the northern North Sea have been explained above by natural processes and there is no need to invoke anthropogenic inputs, this in contrast to the concentrations found in the southern North Sea. In other words, the observed concentrations and their variability are deemed to be the natural background, although we cannot firmly rule out a minor anthropogenic component. The more than 10 times higher Zn concentration found in the northern North Sea, compared to the concentration found in the eastern North Atlantic, may also be a result of atmospheric input. As shown by Chester et al. (1993), atmospheric Zn fluxes to the North Sea are a factor of 100 higher than the Cd fluxes and account for 1/3 of the total annual input. The Zn:Cd ratio calculated from these fluxes is 139 and in the same order of magnitude as the ratio's found in the study area. These latter authors have also shown a south–north decrease in the emission of trace metals to the atmosphere from land masses surrounding the North Sea, and that atmospheric fluxes contribute substantially to the total inputs of trace metals to the southern North Sea.

In the latter part of the North Sea, the concentrations are indeed higher (Duinker and Nolting, 1982; Nolting, 1986; Tappin et al., 1995) and some anthropogenic input may become more likely. From the southern North Sea values alone this is hard to prove, simply because no observations exist in the pre-industrial era, while the generally higher concentrations may just as well be due to natural inputs from rivers, the atmosphere and sediments. On the other hand, the elevated concentrations of Cu, Zn and Cd (Zwolsman et al., 1997) in the river Scheldt compared to the more pristine Mississippi and Amazon rivers (Boyle et al., 1982; Shiller and Boyle, 1985; Shiller, 1997) are almost certainly due to pollution sources, and some of these metals will enter into the southern North Sea. The very high concentrations in sediments of the Scheldt estuary are elevated versus those in the open southern North Sea and tend to further indicate metal pollution of the river Scheldt (van Alsenoy et al., 1993).

Lead has been brought into the sea and oceans mainly through automobile exhausts of leaded gasoline vented into the atmosphere. In the early 1980s, the surface water concentrations in the northwest Atlantic Ocean were about 130–160 pM and some 15-fold higher than in the deep waters due to the anthropogenic invasion (Schaule and Patterson, 1983). Moreover, the Pacific surface concentrations were less at about 60–70 pM and in turn higher than

the about 10 pM deep water values. The more than twofold higher Atlantic values are due to the more extensive industrial activity in the region. Since then, the North American emissions from gasoline were largely phased out and the surface water levels in the Sargasso Sea decreased, first rapidly and then slower, to values around 50 pM in 1996 (Wu and Boyle, 1997). The slower decrease in the 1990s has been ascribed to persistent emissions from other industrial sources.

Moreover, the phasing out of leaded gasoline in Europe is lagging behind North America. As a result, the Pb in unfiltered surface waters of the northeast Atlantic Ocean in 1989/1990 was higher at about 200 pM, as compared to about 80 pM south of the equator (Pohl et al., 1993). Similarly, for our survey area in 1993 the dissolved Pb varies in the 30–200 pM range (Fig. 6) with mean value in each region at 88 pM, 114 pM and 135 pM (Table 3). These are equal to twofold higher than the 60–80 pM observed in 1993 in the Sargasso Sea (Wu and Boyle, 1997). Nevertheless, our 1993 values tend to be twofold lower than the 1981 observations of dissolved Pb around 300 pM in the northern North Sea (Brügmann et al., 1985), when disregarding the variability in both data sets. Similarly, a maximum of Pb in unfiltered samples at about 400 pM had previously been found in the central North Sea, with minimum values of 150 pM in the northern region where our study has now taken place (Dicke et al., 1987). The decreasing trend in our values versus those observed previously in the North Sea in the 1980s needs confirmation in future cruises, but would be consistent with the reduced emissions as well as the decreasing trend observed elsewhere (Wu and Boyle, 1997).

5. Conclusions

Concentrations of Ni, Cu, Cd and Pb in and around a bloom of the coccolithophore *E. huxleyi* in the northern North Sea belong to the lowest values reported thus far for this region, and are comparable with those values found in the northeastern Atlantic Ocean. This is consistent with the major exchange of water masses between North Atlantic and northern North Sea and implies minor sources or sinks in this part of the North Sea. The bloom in itself had no distinct effect on the dissolved metals, except for some removal of Cd within the bloom as shown by its correlation with removal of nitrate.

Concentrations of Zn are, however, a factor of 10 to 20 higher than those found in Atlantic waters. This appears consistent with the concept that the North Sea with adjacent estuaries is a mixing zone of continental sources with high ratio Zn:Cd at 600–900 and the oceanic endmember with a low ratio Zn:Cd at 5–10. The major underlying mechanism is probably the 21-fold higher inorganic complexation of Cd in seawater (due to strong chloride complexes) supporting a 21-fold longer oceanic residence time of Cd. Other processes may conceivably play a role in fractionating Zn from Cd, but their overall effect is yet to be assessed. These processes are the precipitation of sulfides in estuaries and coastal seas with high organic loading, the competition between dissolved organic complexes and particulate adsorbing surfaces in the open water column, and the preferential biological uptake of Zn when indeed only Zn and not Cd is an essential element for marine plankton. Fractionation due to preferential chemical weathering of Cd from crustal source rocks may also be hypothesized and needs further investigations. Moreover, atmospheric inputs of Zn cannot be ignored as an important factor to explain the increased Zn concentrations in the northern North Sea.

The dissolved Pb around 100 pM in 1993 in the northern North Sea is among the lowest values reported for this region thus far, and may well indicate a trend to lower inventories due to reduced industrial emissions. The concentrations of other metals Ni, Cu and Cd are consistent with natural abundances and processes. For these metals, anthropogenic input is not discernible in the northern North Sea.

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